

MENT COOPERATION TRE, Y

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 05 January 2000 (05.01.00)	in its capacity as elected Office
International application No. PCT/NO99/00116	Applicant's or agent's file reference 6 5026-TH
International filing date (day/month/year) 07 April 1999 (07.04.99)	Priority date (day/month/year) 08 April 1998 (08.04.98)
Applicant COLLECTOR, A. Ltd.	

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

04 November 1999 (04.11.99)

in a notice effecting later election filed with the International Bureau on:

2. The election was

1

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p>	<p>Authorized officer</p>
	<p>R. E. Stoffel</p>
<p>Facsimile No.: (41-22) 740.14.35</p>	<p>Telephone No.: (41-22) 338.83.38</p>

ATENT COOPERATION TR! FY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

MARSDEN, J., C.
Frank B. Dehn & Co.
179 Queen Victoria Street
London, EC4V 4EL
ROYAUME-UNI

Date of mailing (day/month/year)
09 August 2000 (09.08.00)

Applicant's or agent's file reference
6 5026-TH

IMPORTANT NOTIFICATION

International application No.

PCT/NO99/00116

International filing date (day/month/year)

07 April 1999 (07.04.99)

1. The following indications appeared on record concerning:

the applicant the inventor the agent the common representative

Name and Address
BOREALIS A/S Lyngby Hovedgade 96 DK-2800 Lyngby Denmark

State of Nationality	State of Residence
DK	DK
Telephone No.	
Facsimile No.	
Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

the person the name the address the nationality the residence

Name and Address
BOREALIS TECHNOLOGY OY P.O. Box 330 FIN-06101 Porvoo Finland

State of Nationality	State of Residence
FI	FI
Telephone No.	
Facsimile No.	
Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

Authorized officer
A. Karkachi
Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)Date of mailing (day/month/year)
22 September 2000 (22.09.00)To:

TANDBERGS PATENTKONTOR AS
Boks 7085
N-0306 Oslo
NORVÈGEApplicant's or agent's file reference
6 5026-TH

IMPORTANT NOTIFICATION

International application No.
PCT/NO99/00116International filing date (day/month/year)
07 April 1999 (07.04.99)

1. The following indications appeared on record concerning:

 the applicant the inventor the agent the common representative

Name and Address

MARDSEN, J., C.
Frank B. Dehn & Co.
179 Queen Victoria Street
London, EC4V 4EL
United Kingdom

State of Nationality

State of Residence

Telephone No.

44 20 7206 0600

Facsimile No.

44 20 7206 0700

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

 the person the name the address the nationality the residence

Name and Address

TANDBERGS PATENTKONTOR AS
Boks 7085
N-0306 Oslo
Norway

State of Nationality

State of Residence

Telephone No.

47 23 19 94 00

Facsimile No.

47 23 19 94 01

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

 the receiving Office the designated Offices concerned the International Searching Authority the elected Offices concerned the International Preliminary Examining Authority other:The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Sean Taylor

Facsimile No.: (41-22) 740.14.35

Telephone No.: (41-22) 338.83.38

'ATENT COOPERATION TR. TY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

Date of mailing (day/month/year)
09 August 2000 (09.08.00)

To:
MARSDEN, J., C. Frank B. Dehn & Co. 179 Queen Victoria Street London, EC4V 4EL ROYAUME-UNI

Applicant's or agent's file reference 6 5026-TH	IMPORTANT NOTIFICATION
International application No. PCT/NO99/00116	International filing date (day/month/year) 07 April 1999 (07.04.99)

1. The following indications appeared on record concerning:		
<input type="checkbox"/> the applicant <input type="checkbox"/> the inventor <input checked="" type="checkbox"/> the agent <input type="checkbox"/> the common representative		
Name and Address TANDBERGS PATENTKONTOR AS Boks 7085 N-0306 Oslo Norway	State of Nationality	State of Residence
	Telephone No. 47 23 19 94 00	
	Facsimile No. 47 23 19 94 01	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input checked="" type="checkbox"/> the person <input checked="" type="checkbox"/> the name <input checked="" type="checkbox"/> the address <input type="checkbox"/> the nationality <input checked="" type="checkbox"/> the residence		
Name and Address MARSDEN, J., C. Frank B. Dehn & Co. 179 Queen Victoria Street London, EC4V 4EL United Kingdom	State of Nationality	State of Residence
	Telephone No. 44 20 7206 0600	
	Facsimile No. 44 20 7206 0700	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:
<input checked="" type="checkbox"/> the receiving Office <input type="checkbox"/> the designated Offices concerned <input type="checkbox"/> the International Searching Authority <input checked="" type="checkbox"/> the elected Offices concerned <input checked="" type="checkbox"/> the International Preliminary Examining Authority <input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer A. Karkachi Telephone No.: (41-22) 338.83.38
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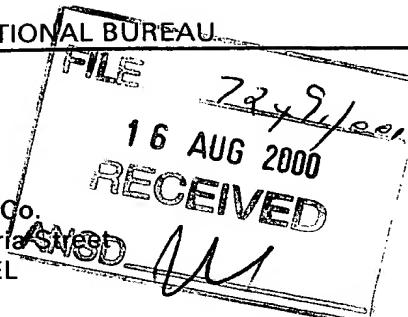
PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

MARDEN, J., C.
Frank B. Dehn & Co.
179 Queen Victoria Street
London, EC4V 4EL
ROYAUME-UNI

Date of mailing (day/month/year) 09 August 2000 (09.08.00)	
Applicant's or agent's file reference 6 5026-TH	IMPORTANT NOTIFICATION
International application No. PCT/NO99/00116	International filing date (day/month/year) 07 April 1999 (07.04.99)

1. The following indications appeared on record concerning:

the applicant the inventor the agent the common representative

Name and Address BOREALIS A/S Lyngby Hovedgade 96 DK-2800 Lyngby Denmark	State of Nationality DK	State of Residence DK
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

the person the name the address the nationality the residence

Name and Address BOREALIS TECHNOLOGY OY P.O. Box 330 FIN-06101 Porvoo Finland	State of Nationality FI	State of Residence FI
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer A. Karkachi Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

17 JAN 2000

From the INTERNATIONAL BUREAU

PCT

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing (day/month/year)
05 January 2000 (05.01.00)

To:

TANDBERGS PATENTKONTOR AS
Boks 7085
N-0306 Oslo
NORVÈGE

Applicant's or agent's file reference 6 5026-TH		IMPORTANT INFORMATION	
International application No. PCT/NO99/00116	International filing date (day/month/year) 07 April 1999 (07.04.99)	Priority date (day/month/year) 08 April 1998 (08.04.98)	
Applicant BOREALIS A/S et al			

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP :GH,GM,KE,LS,MW,SD,SL,SZ,UG,ZW

EP :AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE

National :AU,BG,BR,CA,CN,CZ,DE,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA :AM,AZ,BY,KG,KZ,MD,RU,TJ,TM

OA :BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG

National :AL,AM,AT,AZ,BA,BB,BY,CH,CU,DK,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MW,MX,PT,SD,SG,SI,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZW

3. The applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until **31 months from the priority date** for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: R. E. Stoffel Telephone No. (41-22) 338.83.38
Facsimile No. (41-22) 740.14.35	

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

PCT/IPEA/409

Applicant's or agent's file reference 65026 - TH	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NO99/00116	International filing date (day/month/year) 07.04.1999	Priority date (day/month/year) 08.04.1998
International Patent Classification (IPC) or national classification and IPC7 C 08 F 4/78, C 08 F 10/00		
Applicant Borealis A/S et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 04.11.1999	Date of completion of this report 07.07.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Helena Danielsson/EÖ Telephone No. 08-782 25 00

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/NO99/00116

I. Basis of the report

1. This report has been drawn on the basis of (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

the international application as originally filed.

the description, pages 1-21, as originally filed,
pages _____, filed with the demand,
pages _____, filed with the letter of _____,
pages _____, filed with the letter of _____.

the claims, Nos. _____, as originally filed,
Nos. _____, as amended under Article 19,
Nos. _____, filed with the demand,
Nos. 1-12, filed with the letter of 08.06.2000,
Nos. _____, filed with the letter of _____.

the drawings, sheets/fig --, as originally filed,
sheets/fig _____, filed with the demand
sheets/fig _____, filed with the letter of _____,
sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

the description, pages _____

the claims, Nos. _____

the drawings, sheets/fig _____

3. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/NO99/00116

V. Resoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-12	YES
	Claims		NO
Inventive step (IS)	Claims	1-12	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-12	YES
	Claims		NO

2. Citations and explanations

The claimed invention relates to a catalyst system for the polymerisation of ethylene and a method for the preparation of the catalyst system.

Claims have been amended with the letter of 08.06.2000.

Claim 1 has been restricted to a catalyst system comprising chromium oxide and a metallocene supported on an inorganic support.

The object of the invention is to provide a new catalyst system for the production of a branched polyethylene from ethylene without any addition of comonomer during the polymerisation. Further, it is an object to control the polymerisation reaction to produce polyethylene having desired density and molecular weight

This is accomplished by a catalyst system comprising chromium oxide and a metallocene compound containing zirconium supported on same inorganic support. The chromium in the chromium oxide is in a reduced oxidation state and the support is a particulate inorganic oxide.

The documents cited in the International Search Report were:

- D1) WO 9708213 A1
- D2) WO 9727225 A1
- D3) EP 0339571 A1

..../....

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V

Document D1 relates to polyethylene, which can be obtained by polymerisation of ethylene in the presence of a catalyst system. The catalyst system comprises a Phillips catalyst and a solid containing a constituent derived from a metallocene complex, such as bis-cyclopentadienyl zirconium dichloride. The Phillips catalyst and metallocene are not carried on the same support. The claimed invention differs from the catalyst system disclosed in D1 in that chromium oxide compound and the metallocene compound is supported on the same inorganic support.

Further, in D2 a catalyst system used for the polymerisation of ethylene is disclosed. The first constituent of the catalyst system comprises chromium oxide, where the chromium is in a reduced oxidation state. The other constituent comprises a bis-cyclopentadienyl chromium compound, which is reacted with an inorganic support. The produced polyethylene has an especially broad molecular weight distribution and exhibit particularly good environmental stress cracking resistance. The difference between the claimed invention and this document is that the disclosed system in D2 consists of two independent catalysts.

Document D3 relates to preparation of ethylene polymers in the presence of a catalyst. The catalyst comprises a titanium- or chromium-containing porous inorganic oxide carrier, a transition compound containing a metallocene as a ligand; and an aluminoxane. The difference between the claimed invention and this document is that the system disclosed in D3 consists of two independent catalysts.

It should be observed that claim 4, which relates to a catalyst system according to claims 1 to 3, discloses an unsubstituted cyclopentadienyl. This seems not to be in agreement with claim 2, which relates to a cyclopentadienyl compound substituted with radicals. Therefore, claim 4 should be reformulated.

In view of the above, the catalyst system claimed in claims 1-12 of the invention is considered to fulfil the requirements of novelty, technical applicability and inventive step.

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

TANDBERGS PATENTKONTOR AS
Boks 7085
N-0306 Oslo
NORVÈGE

29 OKT. 1999

Date of mailing (day/month/year) 21 October 1999 (21.10.99)		
Applicant's or agent's file reference 6 5026-TH		IMPORTANT NOTICE
International application No. PCT/NO99/00116	International filing date (day/month/year) 07 April 1999 (07.04.99)	Priority date (day/month/year) 08 April 1998 (08.04.98)
Applicant BOREALIS A/S et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

AU,CN,EP,IL,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CU,CZ,DE,DK,EA,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,
ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,RU,SD,
SE,SG,SI,SK,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
21 October 1999 (21.10.99) under No. WO 99/52951

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer J. Zahra Telephone No. (41-22) 338.83.38
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Continuation of Form PCT/IB/308

**NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF
THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES**

Date of mailing (day/month/year) 21 October 1999 (21.10.99)	IMPORTANT NOTICE
Applicant's or agent's file reference 6 5026-TH	International application No. PCT/NO99/00116

The applicant is hereby notified that, at the time of establishment of this Notice, the time limit under Rule 46.1 for making amendments under Article 19 has not yet expired and the International Bureau had received neither such amendments nor a declaration that the applicant does not wish to make amendments.

E-E
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C08F 4/78, 10/00		A1	(11) International Publication Number: WO 99/52951 (43) International Publication Date: 21 October 1999 (21.10.99)
(21) International Application Number: PCT/NO99/00116		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 7 April 1999 (07.04.99)			
(30) Priority Data: 19981631 8 April 1998 (08.04.98)		NO	
(71) Applicant (for all designated States except US): BOREALIS A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK).			
(72) Inventors; and (75) Inventors/Applicants (for US only): FOLLESTAD, Arild [NO/NO]; Damstien 10, N-3960 Stathelle (NO). JENS, Klaus-Joachim [DE/NO]; Kjærlyghetsstien 19, N-3970 Langesund (NO). BLOM, Richard [NO/NO]; Sørbyhaugen 30, N-0377 Oslo (NO). DAHL, Ivar, Martin [NO/NO]; Kongsberggt. 6, N-0468 Oslo (NO).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(74) Agent: TANDBERGS PATENTKONTOR AS; Boks 7085, N-0306 Oslo (NO).			
(54) Title: CATALYST SYSTEM FOR ETHYLENE POLYMERISATIONS			
(57) Abstract <p>A catalyst system for the polymerisation of ethylene, comprising a particulate inorganic oxide supporting a chromium oxide being in a reduced oxidation state and a metallocene compound having the formula $Cp_2ZrR'R''$, wherein each Cp, being equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independent of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms; or R' or R'' may be a halide. The catalyst system is prepared by a method comprising the steps of calcining the support, joining onto the surface of the support a chromium-organic compound, subjecting the obtained catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state, reducing the oxidised chromium to obtain a main part thereof in a bivalent oxidation state, and contacting the reduced catalyst with the metallocene compound.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
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AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
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DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CATALYST SYSTEM FOR ETHYLENE POLYMERISATIONS

TECHNICAL FIELD

The present invention relates to a supported chromium oxide catalyst, in particular a catalyst system comprising an inorganic support, a chromium oxide and a metallocene compound, and a method for the preparation of said catalyst system. The catalyst produces branched polyethylenes without the use of a copolymer, and the molecular weight can be controlled by feeding hydrogen.

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BACKGROUND ART

To obtain linear polyolefins having desired properties, different catalyst systems in combinations with controlled polymerisation conditions are used. A typical supported chromium catalyst that is extensively used in commercial polymerisations of ethylene is formed by depositing a chromium compound onto a support, which is then oxidised. The oxidised catalyst precursor may be introduced as such into a polymerisation reactor, where it will be reduced *in situ* by the olefin monomers to its active catalytic state. It is also well known that oxidised chromium compounds may be prereduced by suitable reagents, such as hydrogen or carbon-monoxide (J.P. Hogan, *J. Polym. Sci.*, PtA-1, 8, 2637 (1970), and references therein). The resulting chromium surface species are generally accepted to be highly reactive. A prereduced chromium-based catalyst will produce polyethylenes having a broad molecular weight distribution (MWD) and mainly long, straight chains. Such catalysts are not hydrogen-sensitive.

Another commercially important class of catalysts used to polymerise α -olefins are the cyclopentadienyl transition metal catalysts, usually termed metallocene catalysts. Metallocenes contacted with Lewis acids will give effective polymerisation catalysts that produce linear polyethylenes having a narrow molecular weight distribution (MWD). Such catalysts are sensitive to the presence of hydrogen.

By adding comonomers and optionally hydrogen during the catalysed polymerisation reactions the density and chain branching of the produced polymer can be controlled. In the prior art efforts have

been made to develop combined catalyst systems that produce short chain branched polyethylenes, without the addition of comonomers during the polymerisation reactions.

5 US Patent 4,735,931 discloses a catalyst system prepared by first depositing a chromium compound on a predominantly silica support, activating said catalyst in an oxygen-containing atmosphere and thereafter subjecting the thus activated composition to reduction with carbon monoxide. The resulting 10 chromium catalyst composition is then precontacted with a cocatalyst selected from trialkyl boron and dialkyl aluminium alkoxide compounds, preferably triethyl borane, and thereafter contacted with ethylene. When used in olefin polymerisations this catalyst provides in situ generation of comonomers, resulting in 15 tough, flexible, mainly pure polyethylene resins.

US Patent 5,032,651 teaches the use of catalyst mixtures of two transition metal catalysts. One of the catalysts comprises chromium oxide supported on an aluminophosphate, and the other 20 one comprises a β -stabilized tetrahydrocarbyl zirconium compound supported on an inorganic material. The catalysts may be premixed before use, or they may be fed separately to the reactor. Olefinic polymers exhibiting high environmental stress crack resistance (ESCR) are produced.

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EP 206794 describes an olefin polymerisation catalyst comprising a support contacted with a Group 4b, 5b or 6b metallocene and an aluminoxane.

30 EP 088 562 discloses a modified polymerisation catalyst comprising a silica support with deposited chromium. Following oxidation in dry air, the chromium is modified by being contacted with a transition metal compound of Ti, V or Cr, preferably Ti. Only the use of bis-toluene titanium is exemplified, and the 35 obtained polyethylenes have a substantial degree of branching and a medium or broad molecular weight distribution.

US 3,378,536 discloses a process for the polymerisation of ethylene by the use of a two-component catalyst system consisting

of (a) a chromium compound deposited on e.g. silica, where the chromium being activated in an oxygen-containing gas at a high temperature and then reduced with CO; and (b) chromium or vanadium arene where the arene is an aromatic, optionally substituted C₆ ring. The two catalyst components are preferably fed separately to the polymerisation reactor.

It is well known to a person skilled in the art that the various processing techniques used in the manufacturing of final articles from polyethylene resins require polyethylene grades having specific rheological properties. For instance, in the extrusion blow moulding of containers polyethylenes having a broad MWD and long straight chains are typically used, while in film blowing lower density polyethylenes are preferred.

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It is an object of the present invention to provide a novel catalyst system that produces a branched polyethylene from ethylene without any addition of comonomer during the polymerisation reaction. A further object is to control the polymerisation reaction to produce polyethylenes having a desired density and molecular weight. Another object is to obtain polyethylene resins suitable for use blow moulding and film blowing processing.

It has now been found that a catalyst system comprising a prereduced chromium on silica catalyst that have been contacted with a metallocene compound fulfils the requirements above. The novel catalyst system produces a branched low density polyethylene polymer without any added comonomer. The density and molecular weight (and hence the melt flow index) of the polymer can be controlled by the addition of hydrogen to the reactor.

DISCLOSURE OF INVENTION

The present invention thus provides a catalyst system for the polymerisation of ethylene, comprising chromium oxide supported on an inorganic support, wherein

- a) said support being a particulate inorganic oxide;
- b) the chromium of said chromium oxide being in a reduced oxidation state, and comprising
- c) a metallocene compound having the formula:



wherein each Cp, being equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

The invention also provides a method for the preparation of the catalyst system above, comprising the steps of:

- a) calcining a support being a particulate, inorganic oxide selected from the group comprising alumina, silica, titania, zirconia, magnesia, and combinations thereof,
- b) joining onto the surface of said support a chromium-organic compound to obtain a catalyst precursor,
- c) subjecting said catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state,
- d) subjecting said catalyst precursor to reducing conditions to obtain a prereduced catalyst, thus
- e) reducing the oxidised chromium to obtain the main part thereof in a bivalent oxidation state,
- f) contacting said reduced catalyst with a metallocene compound having the formula:



wherein each Cp, equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

BEST MODES FOR CARRYING OUT THE INVENTION

The catalyst system of the present invention comprises a supported reduced chromium/silica catalyst contacted with a metallocene compound. In general, metallocenes based on zirconium, hafnium and titanium are preferred as metallocene catalysts. By metallocenes are meant compounds in which a metal atom or ion or complex ion is π -bonded by at least one ligand, e.g. by 1, 2 or 3 ligands or ligand components. The π -bonding

ligands in such catalysts may be simple unsubstituted cyclopentadienyl rings, but preferably they will be optionally substituted fused ring systems (e.g. indenyl ligands), substituted cyclopentadienyl rings, optionally substituted bridged bis-cyclopentadienyl ligands or optionally substituted bridged bis fused ring systems (e.g. bis indenyl ligands).

The catalyst support may be any oxide of metals from groups 2, 3, 4, 11, 12, 13 and 14 of the Periodic System of Elements.

10 Preferred metal oxides are magnesia, alumina, titania, zirconia and silica. A particularly preferred catalyst support is silica. Such a silica support must contain not less than 90% pure silica, with the remaining part may consisting of other oxides, such as oxides of aluminium, zirconium, titanium, magnesium and phosphor.

15 The support should consist of particles having preferably a spherical or spheroidal shape and a size from about 10 μm to 150 μm , more preferably from 20 μm to 120 μm , and a particle size distribution from narrow to broad within said ranges.

20 The chromium compound to be impregnated onto the silica support may be an inorganic chromium compound, such as chromium nitrate and chromium oxide, or an organic chromium compound, such as chromium acetate. Other chromium compounds are also useable. The chromium compound can be joined with the support in any way known 25 in the art, such as by coprecipitation with the silica support or addition to a silica gel after its formation, or after that it has been dried. A typical procedure of impregnation comprises the use of a water-soluble compound, or the use of an organo-chromium compound in an anhydrous hydrocarbon solution. The only 30 precondition is that the chromium compound can be oxidized to a chromium oxide. The amount of chromium compound joined with the inorganic support must be sufficient to obtain from 0.1% to 10%, preferably from 0.5% to 2.0%, by weight of chromium, calculated as metallic chromium based on the weight of the supported 35 chromium catalyst. When the impregnation is finished any possible remaining solvent is removed to obtain a dry solid.

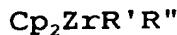
Such solid chromium oxide/silica catalyst precursors are also commercially available from a number of producers. A closer

description of their preparation is therefore regarded as being superfluous.

The obtained catalyst precursor must be activated before use.
5 This is done by calcination in dry air or another oxygen-containing gas at temperatures in the range from 400 to 950 °C, preferably from 550 to 800 °C, during a period from 10 minutes to 24 hours, preferably from 2 to 20 hours. The oxidised catalyst precursor is conventionally subjected to reduction, preferably
10 with carbon monoxide or a mixture of carbon monoxide and an inert component, such as nitrogen or argon. The reduction is normally performed at a temperature within the range from 300 to 500 °C, preferably from 350 °C to 400 °C, during a period from 5 minutes to 48 hours, preferably from 1 to 10 hours. When the reduction
15 is completed, the major part of the contained chromium should preferably be in a bivalent oxidation state. The final chromium catalyst particles should have a surface area from 200 to 600 m²/g, more preferably from 300 to 550 m²/g, and a pore volume from 1 to 3 cm³/g. The chromium oxide/silica catalyst in a
20 reduced state, either as a dry powder or as a slurry in a dry oxygen-free hydrocarbon solvent, e.g. an alkane, must be stored in an inert ambience.

The present invention is not restricted to any particular
25 procedure for the preparation of the chromium oxide/silica catalyst, and other methods than those described here may also be applicable.

The obtained chromium oxide/silica catalyst is contacted with a
30 cyclopentadienyl-zirconium compound, hereinafter termed "zirconocene". Preferred zirconocenes can be represented by the simplified formula:



wherein Cp designates cyclopentadienyl groups selected from
35 unsubstituted cyclopentadienyl; cyclopentadienyl substituted with radicals selected from the group comprising unsubstituted and substituted linear, branched, cyclic or partially cyclic alkyl radicals, and annelated cyclic radicals, containing 1 to 20 carbon atoms; unsubstituted and substituted monocyclic or

polycyclic aryl radicals which optionally also may contain hetero atoms; and aralkyl radicals. The substituents on the cyclopentadienyl ring may also form annelated structures comprising one or more fused benzene, naphtalene or cyclohexene rings, which 5 optionally may contain hetero atoms. The substituents R' and R", equal or different, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms. Preferably, R' and R" are independantly selected from the group 10 comprising methyl, benzyl or fenoxyethyl, and any combination thereof. One or R' and R" may also be a halide, preferably chloride.

A number of suitable metallocene compounds of the formula above 15 are known in the art and have been recited in the literature. Particularly preferred metallocene compounds are embodied in the working examples.

Particularly good results are obtained when Cp represents cyclopentadienyl, and R' and R" are the same and are benzyl or methyl. 20

The zirconocene compound is joined with the activated prereduced chromium oxide/silica catalyst most conveniently by dissolving the zirconocene in a solvent, e.g. toluene, and impregnate the 25 chromium oxide/silica catalyst with this toluene solution. Eventually, the solvent is removed by evaporation, preferably in an inert atmosphere, whereupon the catalyst is ready for use.

The final catalyst will contain both zirconium and chromium, preferably in a molar ratio of zirconium to chromium in the range 30 from 0.1:1 to not higher than 2:1. More preferably the catalyst contains zirconium and chromium in a molar ratio from 0.5:1 to 1:1.

35 Prior to polymerisation, the catalyst may optionally be prepolymerised with a minor amount of ethylene and/or an α -olefin in accordance with methods well known in the art, before being fed continuously to the polymerisation reactor.

Polymerisations can be performed in any conventional type of reactor, such as in a batch reactor or most preferably in a continuous reactor. The present catalysts are suitable for use in all types of olefin polymerisations, including gas phase and suspension polymerisations. In general, polymerisations are performed at temperatures below 110 °C, and at a total pressure in the range from ambient to 50 bar. Hydrogen is used to control the molecular weight, and consequently the melt flow index, of the polymer, whereas the catalyst determines the short chain branching on the polyethylene backbone and hence the density of the polyethylene.

The general polymerisation parameters mentioned above are well known in the art and further details concerning ethylene polymerisations should be superfluous. Typical polymerisation conditions are presented in the examples below.

It is realized that the present catalyst system has its highest catalytic activity when the substituents R' and R" of the zirconocene compound are pure hydrocarbyl radicals, in the examples embodied as benzyl or methyl. A person skilled in the art will understand that similar hydrocarbyl compounds are expected to have the same effect and that such compounds are contemplated by the present invention. The catalysts of this invention provide substantially higher activities than the prior art chromium/-silica catalysts. When the substituents R' and R" contain hetero atoms, such as O and Cl, the present catalysts will get a reduced activity, typically lower than the activity of a comparative prior art chromium/silica catalyst. Thus, the activities of the catalysts of the present invention will be at their highest when the metallocene component is a pure hydrocarbyl zirconocene.

The present catalysts will have an activity that varies with the molar ratio between zirconium and chromium in the final catalyst. When the contained amount of zirconium is higher than the amount of chromium, the catalyst will have a lower catalytic activity than a comparative prior art chromium/silica catalyst. The present catalysts have their highest activity when the molar ratio between zirconium and chromium is about 0.5:1. This indi-

cates that only a minor amount of zirconocene is required to increase substantially the activity of a chromium/silica catalyst.

The catalytic activities of the present catalysts are also influenced by the concentration of hydrogen present in the polymerisation reactor. It has been found that an optimum level is about 1 bar of hydrogen.

The hydrogen level will also influence on the short chain branching of the produced polyethylenes. Analysis of polyethylenes polymerised with the present catalysts show that the obtained polymers have a higher amount of short chain branching than polyethylenes produced with a prior art chromium/silica catalyst. In particular, the amount of ethyl branches will increase. A higher level of hydrogen will increase the amount of short chain branching, in particular when using a catalyst having a ratio Zr/Cr of 0.5. By adjusting this ratio, as well as the hydrogen level inside the reactor, the morphology of the final resin can be controlled. Compared with the common used prior art chromium/silica catalysts, the catalysts of the present invention have a higher activity and will give a higher amount of short chain branching.

The present catalysts are preferably used to homopolymerise ethylene. However, it is also possible to use the present catalysts in copolymerisations of ethylene with a comonomer or a mixture of comonomers. Useful comonomers are all polymerisable α -olefins having the general formula $\text{CH}_2=\text{CHR}$, wherein R is a hydrocarbon radical containing 1-18 carbon atoms, preferably 1-10 carbon atoms. Examples of particularly preferred α -olefins are propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. However, the greatest achievements of the present catalysts are in homopolymerisations of ethylene.

The produced polyethylenes will have a density from 910 to >960 kg/m^3 , and a melt index from 0.01 to above 100 $\text{g}/10 \text{ min}$, preferably from 0.1 to 60 $\text{g}/10 \text{ min}$ (determined according to the method of ASTM 1238), depending on the polymerisation conditions, as explained above. More detailed specifications concerning the pro-

roperties of the obtained polyethylenes are given in the examples.

EXAMPLES

Preparation of a Cr/SiO₂ catalyst

5 A catalyst support of silica having a surface area of 300 m²/g and a pore volume of 1.6 cm³/g was impregnated with an aqueous solution of CrO₃, in an amount sufficient to finally obtain 1 % by weight of Cr, calculated as metal based on the weight of the support. The impregnated support was reduced at 380 °C in a gas 10 consisting of 5% of CO in nitrogen for 4 h, and then allowed to cool to ambient temperature in an inert atmosphere. For further use, the obtained blue-coloured catalyst was suspended in a dry, oxygen-free, purified mineral oil to a level of about 10 % by weight of catalyst.

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Synthesis of bis-cyclopentadienyl-zirconiumbenzyl (Cp₂ZrBz₂).

This zirconocene was prepared according to the method described by Fachinetti et al. in J. Chem. Soc., Chem. Commun., 1972, p. 654, by reacting 3 g of Cp₂ZrCl₂ with 20.6 ml of a 1.0 M solution 20 of BzMgCl (Bz=benzyl) in toluene at 0 °C for 1.5 h. The obtained yellow product was recrystallized from a mixture of toluene/heptane at -25 °C. The crystallized solid was collected by filtration and dried in vacuum.

25 Synthesis of bis-cyclopentadienyl-zirconiummethyl (Cp₂ZrMe₂)

This zirconocene was synthesized according to the method described by Wailes et al. in J. Organomet. Chem., Vol. 34, 1972, p. 155, by reacting 5 g of Cp₂ZrCl₂ with 21.6 ml of MeLi (Me=methyl) in diethylether at 0 °C for 1 h. The precipitated 30 LiCl was removed by filtration and the diethylether evaporated in vacuum to obtain a solid residue. This residue was heated at 80 °C and reduced pressure (2 to 10 torr). The obtained sublimed white crystalline Cp₂ZrMe₂ was collected.

35 Synthesis of bis-cyclopentadienyl-zirconiummethyl(fenoxyethyl) (Cp₂ZrMe(OPhMe))

To 4.84 ml of a 10% toluene solution of Cp₂ZrMe₂ was added a stoichiometric amount of a 2.1% toluene solution of cresol at ambient temperature and allowed to react for 1 h. Methane was

released during the reaction.

Synthesis of bis-cyclopentadienyl-zirconiummethylchloride (Cp₂ZrMe(Cl))

5 To 10 g of a 5% solution of Cp₂ZrMe₂ was added slowly 48.7 ml gaseous HCl at 0 °C. The mixture was then allowed to reach ambient temperature and it was kept at this temperature overnight to complete the reaction.

10 **General procedure for the preparation of zirconocene-containing catalysts**

A synthesized zirconocene compound was contacted with the Cr/SiO₂ catalyst above. In an inert atmosphere at ambient temperature the zirconocene was added dropwise to a 10 % slurry of the Cr/SiO₂ 15 catalyst and the reaction mixture stirred for at least 1 h to complete the reaction.

General polymerisation procedure

A 1 l laboratory stainless steel batch reactor equipped with a 20 paddle stirrer was heated to a desired temperature between 90 °C and 100 °C and purged with nitrogen, then 1.5 ml of the catalyst slurry was introduced and a desired amount of hydrogen was fed to the reactor. Then 0.5 l of i-butane was added to act as a diluent, whereupon ethylene was introduced until a total pressure 25 of 31.0 bar. The overall pressure was kept constant during the entire polymerisation run by feeding ethylene. The reactor temperature was kept constant at the fixed temperature to an accuracy of ±0.5 °C by automatically adjusting the heating and/or cooling of the reactor. Polymerisation times were from 20 and 40 30 minutes.

EXAMPLES 1 TO 8

These examples demonstrate the polymerisation of ethylene in the presence of a catalyst containing one of the various zirconocene 35 compounds synthesised above. The examples show that the catalysts comprising Cr/SiO₂ contacted with Cp₂ZrBz₂ or Cp₂ZrMe₂ have the highest polymerisation activities. In all examples the molar ratio Zr/Cr equalled 1, the polymerisation temperature was in the range from 93 °C to 98 °C, and the H₂ pressure was either 1.0 or

0.5 bar. Polymerisation parameters and obtained results are given in table 1.

EXAMPLES 1 AND 2

5 Polymerisation catalyst: Cr/SiO₂ contacted with Cp₂ZrBz₂.
In a 20 ml vial 0.510 g of the prepared Cr/SiO₂ catalyst (containing 1% Cr) was suspended in 4.168 g of mineral oil and the bottle closed with a septum. By the use of a syringe 0.375 ml of a 10% toluene solution of Cp₂ZrBz₂ was added while stirring 10 by the use of a magnet bar, and the stirring continued for 1 h more. The obtained catalyst was used in the polymerisation of ethylene according to the general polymerisation procedure described above.

15 EXAMPLES 3 AND 4

Polymerisation catalyst: Cr/SiO₂ contacted with Cp₂ZrMe₂.

The procedure of Examples 1 and 2 was followed, except that the catalyst was prepared by adding 0.251 ml of a 10% solution of Cp₂ZrMe₂.

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EXAMPLES 5 AND 6

Polymerisation catalyst: Cr/SiO₂ contacted with Cp₂ZrMe(OPhMe).

The procedure of examples 1 and 2 was followed, except that the catalyst was prepared by adding 0.342 ml of a 10% solution of 25 Cp₂ZrMe(OPhMe).

EXAMPLES 7 AND 8

Polymerisation catalyst: Cr/SiO₂ contacted with Cp₂ZrMe(Cl).

The procedure of examples 1 and 2 was followed, except that the 30 catalyst was prepared by adding 0.342 ml of a 5 % solution of Cp₂ZrMe(OPhMe).

EXAMPLE 9 (COMPARATIVE EXAMPLE)

Polymerisation catalyst: Cr/SiO₂.

35 The procedure of examples 1 and 2 was followed, except that the catalyst was prepared by suspending 2 g of the Cr/SiO₂ prepared above in 16.691 g of mineral oil in a 50 ml glass bottle which was sealed with a septum. An amount of 1.5 ml of the catalyst slurry was withdrawn and used in a polymerisation run.

The results presented in Table 1 show that the pure hydrocarbyl zirconocenes of Examples 1 and 2, Cp_2ZrBz_2 , and 3 and 4, Cp_2ZrMe_2 , gave increased polymerisation activities compared with the standard prior art Cr/Si catalyst. On the other hand, the catalysts of Examples 5 and 6 containing hydrocarboxy substituents, and of Examples 7 and 8 containing chloride substituents, have lower activities than the prior art catalyst of Example 9. Further, the results show that the catalytic activity of the catalyst of Examples 1 and 2 depends on the hydrogen level present during polymerisation, and also properties like MFR and density of the produced polyethylene vary with the hydrogen concentration. Thus, the properties of the produced polyethylene can be controlled by regulating the hydrogen feed to the polymerisation reactor. The catalyst of Examples 3 and 4 shows the same tendency, but less pronounced. The activities of the catalysts of Examples 5 and 6, and 7 and 8, show a much less response to the presence of hydrogen.

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TABLE 1
Polymerisation of ethylene in the presence of catalyst Cr/silica + $\text{Cp}_2\text{ZrR}'\text{R}''$

Ex.	R'	R''	Zr/Cr	H_2 (bar)	Temp. (°C)	Activity g/g·h	MFR g/10 min	Density g/cm ³
Ex. 1	Bz	Bz	1	0.5	93	1054	0.09	0.933
Ex. 2	Bz	Bz	1	1.0	98	788	0.35	0.945
Ex. 3	Me	Me	1	0.5	93	1005	0.006	0.946
Ex. 4	Me	Me	1	1.0	94	849	0.017	0.947
Ex. 5	Me	OPhMe	1	0.5	93	338	0.004	0.952
Ex. 6	Me	OPhMe	1	1.0	97	341	0.03	0.952
Ex. 7	Me	C1	1	0.5	93	383	0.01	0.950
Ex. 8	Me	C1	1	1.0	97	392	0.05	0.047
Comp. 9	-	-	-	1.0	97	617	0.09	0.949

EXAMPLES 10 TO 16

These examples demonstrate the relation between catalytic activity and the ratio Zr/Cr of the catalyst in the polymerisations of ethylene. The catalyst of Examples 1 and 2, Cp_2ZrBz_2 , and of Examples 3 and 4, Cp_2ZrMe_2 , were used. The general polymerisation procedure above was followed.

EXAMPLE 10

Polymerisation catalyst: Cr/SiO_2 contacted with Cp_2ZrBz_2 , having a Zr/Cr molar ratio of 0.25:1.

The catalyst was prepared analogous to example 1 by suspending 1.750 g of prereduced 1% by weight Cr/SiO_2 in 14.685 g of mineral oil in a 50 ml glass bottle provided with a septum. To this mixture was added 0.352 ml of 10% by weight Cp_2ZrBz_2 in toluene, and the mixture was stirred for another 1 h. The obtained catalyst was then used in the polymerisation of ethylene.

EXAMPLE 11

The polymerisation catalyst was prepared as in Example 10, except that 0.5 g of Cr/SiO_2 was suspended in 4.801 g of mineral oil in a 20 ml glass bottle, and 0.201 ml of a 10% by weight solution of Cp_2ZrBz_2 in toluene was added to obtain a Zr/Cr ratio of 0.5:1.

EXAMPLE 12

The catalyst was prepared as in Example 11, except that 0.403 ml of a 10% by weight solution of Cp_2ZrBz_2 in toluene was added to obtain a Zr/Cr molar ratio of 1:1.

EXAMPLE 13

The catalyst was prepared as in Example 11, except that 0.806 ml of a 10% by weight solution of Cp_2ZrBz_2 in toluene was added to obtain a Zr/Cr molar ratio of 2:1.

EXAMPLE 14

Polymerisation catalyst: Cr/SiO_2 contacted with Cp_2ZrMe_2 , having a Zr/Cr molar ratio of 0.5:1.

The catalyst was prepared analogous to example 3 by suspending 1 g of Cr/SiO_2 in 8.327 g of mineral oil in a 50 ml glass bottle

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provided with a septum. To this mixture was added 0.251 ml of a 10% by weight solution of Cp_2ZrMe_2 in toluene, and the mixture was stirred for another 1 h.

⁵ EXAMPLES 15 AND 16

The catalyst was prepared as in Example 14, except using 0.502 ml and 1.004 ml of the 10% by weight solution of Cp_2ZrMe_2 in toluene, respectively. The Zr/Cr ratios were 1:1 and 2:1, respectively.

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The results presented in Table 2 show that the catalyst Cp_2ZrBz_2 of Examples 10 to 13 has a highest activity with a Zr/Cr molar ratio of about 0.5:1. When this ratio is increased, the catalyst activity decreases and becomes zero at a ratio of 2:1. The catalyst Cp_2ZrMe_2 shows a decreasing activity with increasing ratio Zr/Cr from 0.5:1 to 2:1. Thus, for both catalysts an optimal ratio seems to be Zr/Cr = 0.5:1.

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TABLE 2

Polymerisation of ethylene in the presence of catalyst
 Cr/silica + Cp₂ZrR₂ with various Zr/Cr molar ratios

Ex.	R, R''	Zr/Cr	H ₂ (bar)	Temp. (°C)	Activity g/g·h	MFR g/10 min	HLMFR g/10 min
Ex. 10	Bz	0,25	2	93	1115	0.087	16
Ex. 11	Bz	0,5	0.5	94	1656	0.088	13.75
Ex. 12	Bz	1	0.5	93.5	1282	0.034	7.93
Ex. 13	Bz	2	1	95.3	0	-	-
Ex. 14	Me	0,5	0.5	4	1174	0.029	6.02
Ex. 15	Me	1	0.5	94	970	0.014	4.06
Ex. 16	Me	2	0.5	93.6	525	0.021	4.63
Comp. 9	-	-	1	97	617	0,091	14,5

EXAMPLES 17 TO 22

These examples demonstrate the effect of varying the partial pressure of hydrogen in the reactor when polymerising ethylene in the presence of catalysts Cp_2ZrBz_2 and Cp_2ZrMe_2 . In 5 all examples the molar ratio Zr/Cr equalled 0.5:1. Polymerisation parameters and obtained results are given in Table 3.

EXAMPLES 17 TO 20

Polymerisation catalyst: Cr/SiO₂ contacted with Cp_2ZrBz_2 .

10 The catalyst was prepared analogous to example 11 by suspending 1.501 g of reduced 1% by weight of Cr/SiO₂ in 12.473 g of mineral oil in a 50 ml glass bottle provided with a septum. To this mixture was added 0.603 ml of a 10% by weight solution of Cp_2ZrBz_2 in toluene and the mixture was stirred for another 1 h. The 15 obtained catalyst was then used in the polymerisation of ethylene according to the general polymerisation procedure outlined above, with hydrogen pressures of 0, 0.5, 1 and 2 bars, respectively.

EXAMPLES 21 AND 22

20 Example 14 was repeated, except that the hydrogen pressure was 1 bar and 2 bars, respectively.

The results presented in Table 3 show that catalyst Cp_2ZrBz_2 and catalyst Cp_2ZrMe_2 behave differently in the presence of hydrogen. 25 Catalyst Cp_2ZrBz_2 used in Examples 17 to 21 has a higher activity around 1 bar hydrogen pressure. Increased hydrogen level increases the melt index and lowers the density of the produced polyethylene, which indicates an increasing amount of short chain branching. Catalyst Cp_2ZrMe_2 used in Examples 14, 21 and 22 30 responds very little to an increased hydrogen pressure.

TABLE 3
 Polymerisation of ethylene in the presence of catalyst
 Cr/silica + Cp₂ZrR₂ (Zr/Cr molar ratio 0.5) at increasing H₂ levels

Ex.	R, R"	H ₂ (bar)	Temp. (°C)	Activity g/g·h	MFR 9/10 in	HLMFR g/10 min	Density g/cm ³
Ex. 17	Bz	0	92,8	923	0,06	8,9	0,937
Ex. 18	Bz	0,5	93	1290	0,15	19,8	0,937
Ex. 19	Bz	1	93,2	1413	0,2	28,2	0,934
Ex. 20	Bz	2	93	1057	1,07	87,6	0,928
Ex. 14	Me	0,5	94	1174	0,029	6,02	0,948
Ex. 21	Me	1	94	1190	0,021	5,89	0,948
Ex. 22	Me	2	94	948	0,034	8,93	0,946
Ex. 9		1	97	617	0,091	14,5	0,949

EXAMPLE 23

Example 11 was repeated, except that the level of hydrogen was increased to 1 bar.

5 EXAMPLE 24

Example 12 was repeated, except that the level of hydrogen was increased to 1 bar.

Polyethylenes produced with catalyst Cr/SiO₂ + Cp₂ZrBz₂ were subjected to spectroscopic analysis of end groups with IR and ¹³C-NMR. The spectroscopic analysis shows that the branches are mainly ethyl and butyl branches which have been introduced by the copolymerisation of 1-butene and 1-hexene as comonomers produced from ethylene simultaneously with the polymerisation reaction in the reactor. Obtained results are presented in Table 4.

The results of Table 4 show that there is produced a considerable amount of short chain branching on the polyethylenes during polymerisation. The short chain branching can be controlled by using catalysts with different Zr/Cr ratios and by adjusting the hydrogen level.

Table 4
Polymerization of ethylene in the presence of catalyst $\text{Cr/SiO}_2 + \text{Cp}_2\text{ZrBz}_2$

Ex.	Zr/Cr mol/mol	H_2 (bar)	Temp. (°C)	MI g/10 min	Density g/10 min	Methyl ¹⁾ pr. 1000 °C	Vinyl ¹⁾ pr. 1000 °C	Trans ¹⁾⁽²⁾ pr. 1000 °C	Ethyl ³⁾ pr. 1000 °C	Butyl ³⁾ pr. 1000 °C
Ex. 11	0,5	0,5	94	0,09	0,945	4,2	0,89	0,016	2,0	1,7
Ex. 23	0,5	1	97	0,82	0,935	8,3	0,91	0,021	4,0	4,6
Ex. 12	1	0,5	93,5	0,03	0,94	3,7	0,81	0,02	2,4	1,8
Ex. 24	1	1	97	0,35	0,945	5,5	0,95	0,028	1,8	2,0
Comp. 9		1	97	0,09	0,949	1,3	0,87	0,002	0,3	0,3

- 1) From IR measurements
- 2) Transvinylene fragments
- 3) From ^{13}C -NMR measurements

C L A I M S

1. A catalyst system for the polymerisation of ethylene,
5 comprising chromium oxide supported on an inorganic support,
characterised by:

- a) said support being a particulate inorganic oxide;
- b) the chromium of said chromium oxide being in a reduced oxidation state,

10 and comprising

- c) a metallocene compound having the formula:



wherein each Cp , being equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'' ,
15 independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

20 2. A catalyst system according to claim 1, characterised in that the cyclopentadienyl compound is substituted with radicals selected from the group comprising unsubstituted and substituted linear, branched, cyclic or partially cyclic alkyl radicals and annelated cyclic radicals, containing 1 to 20 carbon atoms; un-
25 substituted and substituted monocyclic or polycyclic aryl radicals which optionally also may contain hetero atoms; and aralkyl radicals; the substituents on the cyclopentadienyl ring may also form annelated structures comprising one or more fused benzene, naphtalene or cyclohexene rings, which optionally may
30 contain hetero atoms, and the two cyclopentadienyl rings may also be connected through a bridge.

3. A catalyst system according to claim 1, characterised in that R' and R'' are selected from the group comprising chloride,
35 methyl, benzyl or phenoxyethyl, and combinations thereof.

4. A catalyst system according to claims 1 to 3, characterised in that Cp is an unsubstituted cyclopentadienyl and that R' and R'' are equal and are either methyl or benzyl.

5. A catalyst system according to claims 1 to 4, characterised in that the metallocene is bis-cyclopentadienyl-zirconium dibenzyl.

5 6. A catalyst system according to claim 1, characterised in that said support is a particulate, inorganic oxide selected from the group comprising alumina, silica, titania, zirconia, magnesia, and combinations thereof.

10 7. A catalyst system according to claim 6, characterised in that said support is silica having the shape of spherical or spheroidal particles with a particle size in the range of from 20 μm to 150 μm , and a surface area from 200 m^2/g to 600 m^2/g .

15 8. A catalyst system according to claim 1, characterised in that the chromium is present in an amount from 0.1 % to 10 % by weight calculated as metallic chromium based on the weight of the chromium/silica catalyst of a) and b).

20 9. A catalyst system according to claim 8, characterised in that the chromium is present in an amount from 0.5 to 2,0 % by weight of chromium.

10. A catalyst system according to claim 1 to 5, characterised by a molar ratio between zirconium and chromium in the final catalyst in the range from 0.1:1 to not higher than 2:1.

11. A catalyst system according to claim 9, characterised in that said molar ratio between zirconium and chromium is from 30 0.5:1 to 1:1.

12. A method for the preparation of the catalyst system of claim 1, comprising the steps of:

35 a) calcining a support being a particulate, inorganic oxide selected from the group comprising alumina, silica, titania, zirconia, magnesia, and combinations thereof,

b) joining onto the surface of said support a chromium-organic compound to obtain a catalyst precursor,

c) subjecting said catalyst precursor to oxidising

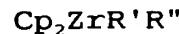
conditions to obtain the chromium in an oxidised state,

d) subjecting said catalyst precursor to reducing conditions to obtain a prereduced catalyst,

characterised by

5 e) reducing the oxidised chromium to obtain the main part thereof in a bivalent oxidation state

f) contacting said reduced catalyst with a metallocene compound having the formula:



10 wherein each Cp , equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'' , independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms,
15 and R' or R'' may be a halide.

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/NO 99/00116**A. CLASSIFICATION OF SUBJECT MATTER****IPC6: C08F 4/78, C08F 10/00**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9708213 A1 (BASF AKTIENGESELLSCHAFT), 6 March 1997 (06.03.97), page 4, line 35 - page 5, line 2; page 8, line 7 - line 18, claims --	1-12
Y	EP 0339571 A1 (SHOWA DENKO KABUSHIKI KAISHA), 2 November 1989 (02.11.89), page 8, line 29 - line 53 --	1-12
Y	WO 9727225 A1 (BOREALIS A/S), 31 July 1997 (31.07.97), page 7, line 7 - page 8, line 15 --	1-12

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

Date of mailing of the international search report

13 August 1999

02-09-1999

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86Authorized officer
Helena Danielsson/ELY
Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00116

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0206794 A1 (EXXON CHEMICAL PATENTS INC.), 30 December 1986 (30.12.86), page 10, line 15 - line 34, claims --	1-12
A	US 3378536 A (DARRELL W. WALKER ET AL), 16 April 1968 (16.04.68), column 2, line 10 - line 14, claims -- -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/07/99

 International application No.
 PCT/NO 99/00116

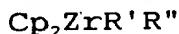
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WO 9727225 A1	31/07/97	AU 1677597 A CN 1209814 A EP 0876406 A NO 300220 B NO 960350 D	20/08/97 03/03/99 11/11/98 28/04/97 00/00/00
EP 0206794 A1	30/12/86	SE 0206794 T3 AR 240463 A AT 111114 T AU 611384 B AU 616396 B AU 624285 B AU 1223488 A AU 5891486 A AU 7007991 A CA 1268754 A DE 3689244 D, T DE 3750506 D, T EP 0275676 A, B EP 0526955 A ES 2058131 T IN 172494 A JP 1501633 T JP 2556969 B JP 2764163 B JP 61296008 A KR 9400788 B US 4808561 A US 4897455 A US 5191052 A WO 8804672 A AT 96812 T BR 8602880 A CS 273318 B CS 8604580 A DK 292486 A FI 862625 A IN 166774 A IN 170390 A MX 168652 B YU 108086 A	30/04/90 15/09/94 13/06/91 31/10/91 04/06/92 15/07/88 24/12/86 11/04/91 08/05/90 05/05/94 12/01/95 27/07/88 10/02/93 01/11/94 04/09/93 08/06/89 27/11/96 11/06/98 26/12/86 31/01/94 28/02/89 30/01/90 02/03/93 30/06/88 15/11/93 17/03/87 12/03/91 12/07/90 22/12/86 22/12/86 14/07/90 21/03/92 02/06/93 31/08/88
US 3378536 A	16/04/68	NONE	

C L A I M S

REPLACED BY
ART 34 AMENDI

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characterised by:

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- 10 and comprising
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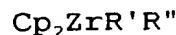
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